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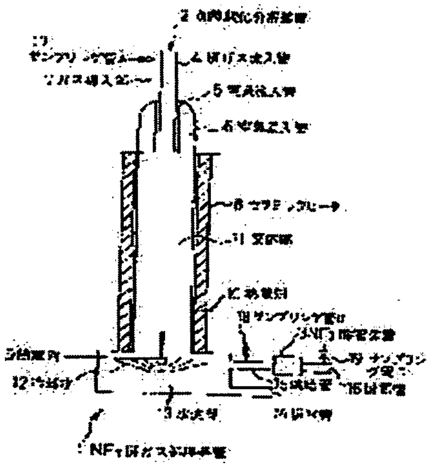
(54) METHOD AND DEVICE FOR TREATING WASTE NF3 GAS

(57)Abstract:

PURPOSE: To remove a harmful gas with high efficiency at a low running cost by heating, oxidizing and decomposing a waste NF3 gas, then removing the oxidizing gas such as hydrofluoric acid and SiO2 at the water washing part and removing the unoxidized NF3, etc., by the metal oxide in an NF3 removal device.

CONSTITUTION: The waste NF3 gas treating device 1 is formed with a heating, oxidizing and decomposing device 2 and an NF3 removal device 3. The waste gas from its inlet pipe 4, nitrogen from its inlet pipe 5 and air from its inlet pipe 6 are introduced into the reaction part 11 of the device 2 to heat, oxidize and decompose the waste gas, and most of the NF3 is oxidized and decomposed. The treated gas contg. the reaction product is washed with cooling water 12 in a washing part 13, and the waste water contg. soluble material such as F2 and SiF4, SiO2, etc., is discharged outside the system. The water-washed gas is introduced into the NF3 removal device 3, the unoxidized NF3, etc., are removed by metal oxides, etc., and the waste gas is purified and made harmless.



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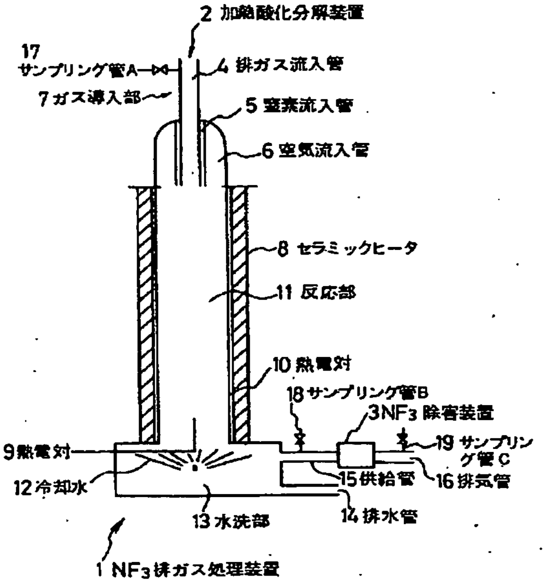
(54)【発明の名称】　ＮＦ３　排ガス処理方法および装置

(57)【要約】

【目的】　本発明の目的は、ランニングコストが低廉で、かつ高い有害ガス除去率を供するNF_3 排ガス処理方法およびこれを適用した装置を提供するものである。

【構成】　本発明の具体的なNF_3 排ガス処理装置１は、加熱酸化分解装置２とNF_3 除害装置３とから構成され、加熱酸化分解装置２の反応部１１に排ガス流入管４からの排ガス、窒素流入管５からの窒素、空気流入管６からの空気とを放出して排ガスを加熱酸化分解することにより、NF_3の大部を酸化分解すると共に生成した加熱酸化分解生成物を含む処理ガスを冷却水１２にて水洗部１３で水洗処理し、F_2 、SiF_4 等の可溶性物質、SiO_2 等を含む排水を系外に排出すると共に水洗処理された処理ガスは該NF_3 除害装置３に導入され、未酸化のNF_3 等が金属酸化物等により除害処理され、排ガスを浄化かつ無害化することができる。



【特許請求の範囲】

【請求項１】　NF_3を含む排ガスを加熱酸化分解処理し、該加熱酸化分解処理したガスに残留するNF_3を除害処理することを特徴とするNF_3排ガス処理方法。

【請求項２】　NF_3を含む排ガスを加熱酸化分解する装置と該加熱酸化分解処理したガスに残留するNF_3を除害処理する除害装置とからなることを特徴とするNF_3排ガス処理装置。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、半導体や液晶の製造などに伴い発生するNF_3排ガスを浄化して無害化する方法およびその装置に関するものである。

【０００２】

【従来の技術】ＣＶＤ排ガスは、未反応のプロセスガスおよびそれの分解で生成する有害成分を多量に含むために処理が必要である。

【０００３】また、ＣＶＤのクリニーニングのために用いるNF_3は、クリーニング排ガスとして未反応のNF_3や反応で生成するSiF_4等が含有され、処理して無害化する必要がある。

【０００４】従来、ＣＶＤ排ガス処理には湿式スクラバーによる吸収法、固体吸着剤での吸着法、燃焼等の方法で処理されてきた。また、NF_3については湿式吸収、熱分解＋吸着等の処理が行われてきた。

【０００５】湿式吸収の場合は、有害ガスの除去率が低い場合が多い。吸着法では除去効率は高いが吸着剤や分解剤の交換が必要でランニングコストが高い。燃焼法は可燃性ガスが対象のＣＶＤ排ガス処理には効果的であるが、クリーニングガスの処理ができない。

【０００６】本発明はランニングコストが低廉で、かつ高い有害ガス除去率を供するものである。

【０００７】

【課題を解決するための手段】本発明は、下記①および②記載の処理方法および装置であり、これにより上記課題を解決できる。

【０００８】①　NF_3を含む排ガスを加熱酸化分解処理し、該加熱酸化分解処理したガスに残留するNF_3を除害処理することを特徴とするNF_3排ガス処理方法。

②　NF_3を含む排ガスを加熱酸化分解する装置と該加熱酸化分解処理したガスに残留するNF_3を除害処理する除害装置とからなることを特徴とするNF_3排ガス処理装置。

【０００９】本発明において、NF_3を含む排ガス、即ちNF_3排ガス（以下、単に排ガスと言う）とは、NF_3を含むガスならいかなるものでもよいが、例えば、半導体製造における少なくともNF_3を含むクリーニングガスを使用する装置における排ガスを意味し、プロセスガスの排ガスに加え、装置内を該クリーニングガスにてクリーニング処理した結果生じた種々のNF_3と装置内部に存在するクリーニングすべき物質との反応生成物をも包含する意味である。従って、本発明においてNF_3を除害処理するとは、NF_3誘導体の除害処理をも包含する意味で使用するものとする。

【００１０】本発明は、排ガスを直接に加熱酸化分解して、プロセスガス由来の排ガスにおいては、実質的に有機部分の大部をCO_2と水とし、金属部分をSiO_2等の金属酸化物微粒子にし、NF_3においてはF_2とNO_x等を生じさせる。次いで、この処理ガスを所望により水洗して可溶化または巻き込みにより、微粒子、F_2、SiF_4等を除去してから、除害剤を充填したNF_3除害装置に通すことにより、残留したNF_3、NO_x等を除去し、無害な処理ガスを得るものである。

【００１１】本発明においては、排ガスを加熱酸化分解して、排ガスに含まれる有機部分を水とCO_2に無害化し、NF_3の大部、好ましくは、８０％以上を酸化することにより、後段の未酸化NF_3の処理量が大幅に低減されるので、NF_3処理の経済性が向上するという利点を有する。

【００１２】本発明において使用される除害剤とは、NF_3がそのまま環境下に放出されるのを防止できる機能を有するものであれば、特に制限されず公知のものが使用できる。具体的な除害剤の例を示せば、NF_3と化学的に反応してNF_3の一部もしくは全部を他の化合物に変化させNF_3を無害化する化学除害剤、NF_3を物理的に吸着させて保持する物理除害剤、これらの併用剤等が挙げられる。

【００１３】化学除害剤としては、NF_3を酸化分解してF_2とNO_xに変化させると共にF_2と化学反応するタイプが挙げられ、好ましくは鉄、マンガン、銅、珪素、チタン等の金属またはその酸化物が挙げられる。

【００１４】物理除害剤としては、シリカ、活性炭、アルミナ、モレキュラーシーブ等が挙げられる。該除害剤の形態は任意であり、糸上、粉末状、他の材料、例えば、セルロース等との複合材料等が使用でき、通常、上記加熱酸化分解処理したガスの流入口とNF_3を除害処理したガスの流出口を設けた容器内に所望量、充填または装填して除害装置を構成することができる。

【００１５】該除害装置の温度は、化学除害剤を使用した場合は３００℃以上の条件で行うことが好ましい。この加熱手段はヒータ等で加熱するのがよいが、処理済排ガスとの熱交換で行うこともできる。

【００１６】また、加熱酸化分解処理されたガスの除害装置における処理速度ＳＶ（流速）は２０００　１／ｈで処理するのが望ましい。本発明における排ガスを排出する装置として、典型的にはＣＶＤ装置が挙げられ、該排ガスは、ＣＶＤ処理時のプロセスガス由来のＣＶＤ排ガスおよび／またはクリーニング時のクリーニング排ガスとから構成される。

【００１７】該ＣＶＤ排ガスを与えるプロセスガスを例

示すれば、無機原料としては、例えば、モノシラン、ジシラン、ジクロルシラン等、有機原料としては、例えば、ＴＥＯＳ（テトラエトキシシラン）、ＴＭＢ（トリメトキシボラン）等があり、これらは１種以上単独または組み合わせて用いられる。これらの排ガスには、これらの未反応物あるいはその誘導体、反応分解物、例えば、H_2、ＣＯ、C_2H_5OH等のアルコール、CH_3CHO等のアルデヒド、C_2H_4等の炭化水素等の加熱酸化分解性物質が含まれ、加熱酸化分解されることにより、主として、SiO_2等の金属酸化物、H_2OとCO_2になる。ここで言う加熱酸化分解とは、分解不能のものの単なる酸化、例えば、水素、金属等の単体の酸化等をも包含することは明らかである。

【００１８】該クリーニング排ガスは、少なくともNF_3とＣＶＤ装置内物質（未排気のＣＶＤ処理済物質等）との反応物、例えば、SiF_4、NF_3誘導体等、およびクリーニングガスとクリーニングガスにより物理的にクリーニングしたＣＶＤ内物質等からなる。

【００１９】クリーニングガスとしては、他にCF_4、C_2F_6、SF_6、ClF_3などが挙げられる。本発明における加熱酸化分解処理の反応条件、排ガスの導入条件等は特に制限されるものではないが、少なくとも酸素の共存下に排ガスに含有される加熱酸化分解性物質が加熱酸化分解されればよい。従って、排ガスを加熱酸化分解装置に導入する時、同時に酸素が加熱酸化反応部に存在することが必要である。この酸素の存在方法は任意であるが、該酸素は通常排ガスと共に酸素含有ガス、例えば、空気等として導入することが好ましい。また、加熱酸化分解の条件を調整するために任意のガスを混在させることができる。例えば、窒素等の不活性ガスを混在させ、該窒素ガスが排ガスを包みかつ酸素がこれらを包むような３層状態で加熱酸化分解装置の反応部に導入されることが好ましく、加熱酸化分解装置にこれらのガス導入部として同心状に管を３層構造にしたものを配備することが好ましい。

【００２０】また、加熱酸化分解処理における加熱手段も任意であるが、好ましくは、上述のように電気的に温度制御可能なヒータ加熱方式が望ましく、通常反応部の壁内に設けることができる。また、反応部の温度は、８００～１０００℃の範囲が好ましい。

【００２１】本発明において、加熱酸化分解処理された排ガスはその組成に応じて、そのままNF_3を除害する除害装置に移行させるか、更に他の任意の処理を加えてから除害装置に移行させることができる。

【００２２】特に、本発明においては加熱酸化分解処理された排ガスを水と接触させること、即ち、水洗処理に供することが好ましく、これにより、該分解処理により生成したSiO_2等の金属酸化物微粒子の巻き込みによる除去、SiF_4、F_2等の水溶性化合物等の可溶化による除去、処理ガスの冷却等を行うことができる。この水洗処理の方法は任意であるが、噴霧状に処理ガスと接触させることが好ましい。

【００２３】この水洗処理されたガスをNF_3除害処理したものは、環境に放出もしくは更に所望により他の任意の処理、例えば、公知の吸着処理等を施すことができ、任意の排気手段、例えば、排気管等を除害装置に配備することができる。また、水洗排水は排水管等の排水手段により系外に排出される。これらの水洗処理手段、排出管等は加熱酸化分解装置に設けても、別途独立して設けてもよい。

【００２４】本発明は、上記処理工程が一連のものとして連続的かつ自動的に行われるようにかつ所望処理条件を適宜選定できるように制御装置を具備することができる。この制御装置は、通常種々の検出装置、例えば、温度、圧力、水位等のセンサーと連絡され、常に安全でしかも最適処理が行えるように構成される。

【００２５】本発明における加熱酸化分解方式は高温下で排ガスを酸化分解するために短時間で処理ができるためにＣＶＤ排ガスが大量であっても除害効率が高く、また、加熱のための電気、空気、窒素、冷却用水（洗浄水を兼ねる）があれば効率よく処理できるので乾式吸着法のみよりランニングコストが低廉である。また、加熱酸化分解装置と必要により水洗部（ガス冷却、固形物除去）とNF_3除害装置を直列につなぐことによって、水洗部で酸性ガスを除去し、その後加熱分解装置で分解できなかったNF_3をNF_3除害装置で完全に除去できる。また、導入したNF_3のうち約８０％が加熱酸化分解装置で除去されるためNF_3除害装置への負荷が大幅に低減できる。

【００２６】

【作用】本発明は、NF_3クリーニングガスを含むＣＶＤプロセス等から排出される排ガスをまず加熱酸化分解装置で処理する。加熱酸化分解装置では８００℃以上１０００℃以下でシラン、ジシランなどのＣＶＤ排ガスおよびNF_3を酸化分解する。

【００２７】次に所望により水洗部でフッ酸等の酸性ガスおよびSiO_2を除去する。最後にNF_3除害装置にて好ましくは３００℃以上に加熱した条件でNF_3を金属酸化物等と反応させ除去することによりＣＶＤ排ガスおよびNF_3クリーニング排ガスを完全に分解除去することができる。

【００２８】

【実施例】本発明の具体的実施例を図１に従って説明するが、本発明はこれにより限定されない。

【００２９】図１は、本発明法に使用される処理装置の一例を示し、本発明のNF_3排ガス処理装置１は、加熱酸化分解装置２とNF_3除害装置３とから構成される。加熱酸化分解装置２は、ＣＶＤ装置からのＣＶＤ排ガスを導入する排ガス流入管４、排ガス酸化を調整するための窒素を導入するための窒素流入管５および排ガス中の

加熱酸化分解性物質を酸化するための酸素を供給するための空気流入管６を同心状に構成した３層構造のガス導入部７と、ガス導入部から放出されるこれら混合ガス中の排ガスを加熱酸化分解するための熱源であるセラミックヒータ８を外壁に有すると共に熱電対９、１０を配備した温度制御されている反応部１１と、反応部１１にて生成した加熱酸化分解生成物を含む処理ガスを冷却水１２にて水洗処理するための水洗部１３とF_2、SiF_4等の可溶性物質、SiO_2等を含む排水を系外に排出する排水管１４から構成される。

【００３０】NF_3除害装置３は、加熱酸化分解装置２の後段に設けられ供給管１５を介して水洗処理された処理ガスが該NF_3除害装置３に導入される。該NF_3除害装置３は、導入されたNF_3等の除害すべきガスを除害処理する金属酸化物等を充填したものであり、ここを通過させることにより排ガスを浄化かつ無害化することができ、これを配備された排気管１６より、排出する。尚、１７～１９は排ガス、加熱酸化分解・水洗処理されたガス、触媒処理されたガスの各サンプリング管Ａ，Ｂ，Ｃである。

【００３１】

【実験例】図１に示した装置を用いて処理試験を行った。NF_3とSiH_4を含む排ガス量は４０Ｌ／分、加熱酸化分解装置の処理条件は反応温度９００℃、N_2 １０Ｌ／分、酸化用空気２０Ｌ／分、冷却水４Ｌ／分とした。NF_3除害装置の反応温度を３００℃とした。その結果を表１に示す。表中、Ａ、Ｂ、Ｃは、サンプリングした管を示す。

【００３２】

【表１】

表-1　単位：ｐｐｍ

	NF_3			SiH_4		
	A	B	C	A	B	C
1 時間	5100	950	< 10	3000	< 5	< 5
2 時間	5000	850	< 10	2800	< 5	< 5
3 時間	5000	1000	< 10	3100	< 5	< 5
4 時間	5000	850	< 10	3000	< 5	< 5

【００３３】表１に示したように加熱酸化分解装置でSiH_4は除去でき、NF_3も８０～８３％除去できる。残留したNF_3を後段のNF_3除害装置で処理することにより、ＣＶＤから発生する排ガスを完全に除害できる。

【００３４】

【発明の効果】本発明の排ガス処理方法により、従来行われていた吸着法に比べてランニングコストの低減および有害ガスの高効率での除去を可能にした。また、本発明ではＣＶＤ排ガスとクリーニング排ガスが完全に分離されずに排出される枚葉式のＣＶＤ装置の排ガスを処理する場合、特に有効である。

【図面の簡単な説明】

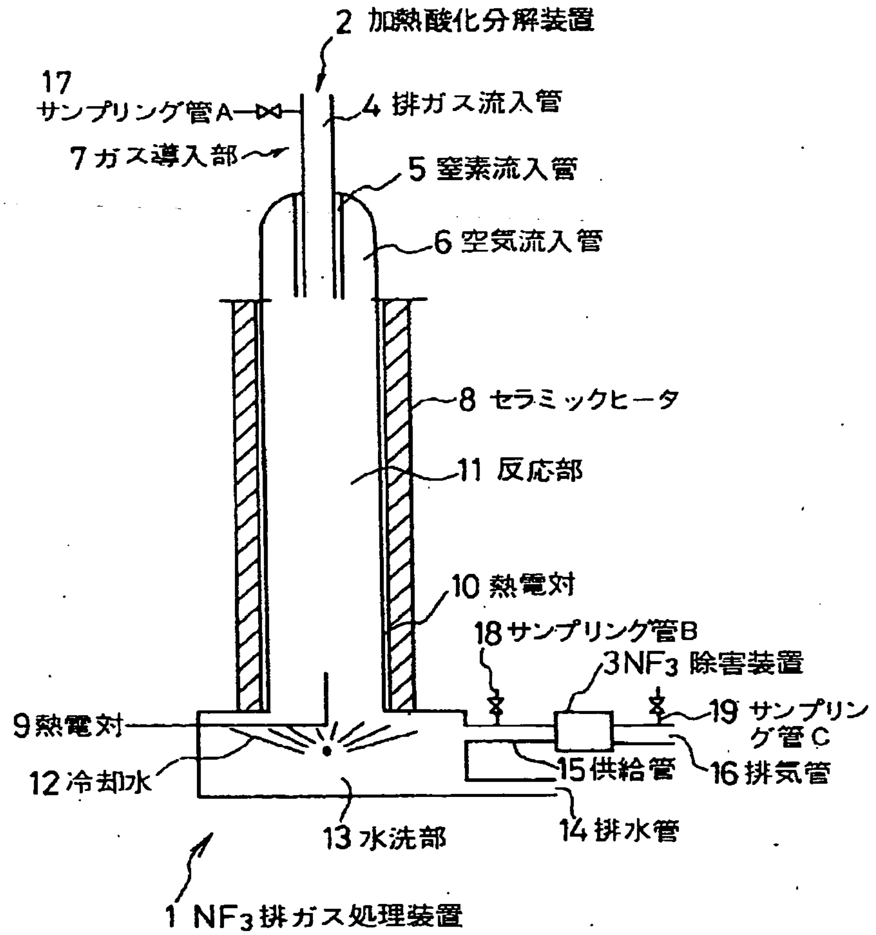
【図１】本発明ほ方法が適用されるNF_3排ガス処理装置を説明するための図である。

【符号の説明】

1	NF_3排ガス処理装置
2	加熱酸化分解装置
3	NF_3除害装置
4	排ガス流入管
5	窒素流入管
6	空気流入管
7	ガス導入部
8	セラミックヒータ
9	熱電対
10	熱電対

12	冷却水
13	水洗部
14	排水管
15	供給管
16	排気管
17	サンプリング管Ａ
18	サンプリング管Ｂ
19	サンプリング管Ｃ

【図１】



Japanese Patent Laid-Open No. 4-290523

[Title of the Invention]

NF$_3$ Waste Gas Treatment Method and System

[Abstract]

[Object]

To provide an NF$_3$ waste gas treatment method and a system to which this method is applied, wherein its running cost is low and its removal rate of toxic gas is high.

[Solving Means]

An NF$_3$ waste gas treatment system 1 according to this invention comprises a thermal oxidative decomposition apparatus 2 and an NF$_3$ detoxing apparatus 3. In this system, waste gas from a waste gas inlet pipe 4, nitrogen from a nitrogen inlet pipe 5, and air from an air inlet pipe 6 are discharged into a reaction part 11 of the thermal oxidative decomposition apparatus 2 to cause the waste gas to be heated, oxidized and decomposed, whereby most of NF$_3$ is oxidized and decomposed, and the gas to be treated containing thermal oxidative decomposable products produced is washed with cooling water 12 at a water washing part 13. Then the waste water containing soluble substances such as F$_2$, SiF$_4$, SiO$_2$, etc. is discharged out of the system and, at the same time, the gas washed with water is fed into the

NF_3 detoxing apparatus 3, and not-yet oxidized NF_3 etc. of the gas is removed and treated by using metal oxide etc. to purify and make non-toxic the waste gas.

[Claims]

[Claim 1]

An NF_3 waste gas treatment method characterized in that waste gas containing NF_3 is subjected to a thermal oxidative decomposition treatment and NF_3 remaining in the gas treated is detoxed.

[Claim 2]

An NF_3 waste gas treatment system characterized by comprising an apparatus for subjecting a waste gas containing NF_3 to a thermal oxidative decomposition treatment and a detoxing apparatus for detoxing NF_3 remaining in the gas treated.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to a method and apparatus for purifying and detoxing NF_3 waste gas generated in a manufacturing process of a semiconductor or liquid crystal.

[0002]

[Prior Art]

CVD waste gas requires to be treated because it contains a great amount of unreacted process gas and harmful ingredients generated in its decomposing action.

[0003]

In addition, NF_3 used for cleaning in CVD contains unreacted NF_3 acting as a cleaning waste gas, SiF_4 generated through reaction, etc. Therefore, NF_3 is required to be treated and be non-toxic.

[0004]

Conventionally, a CVD waste gas has been treated by an absorbing method performed by a wet-type scrubber, an adsorption method performed with a solid adsorbing agent, a combustion method, and the like are applied. In addition, NF_3 has been treated with a combination of the wet-type absorption process or thermal decomposition and adsorption process.

[0005]

The wet-type absorption process sometimes has a low removal rate of harmful gas. Although the adsorption method has a high removal rate, it is requested that an adsorption agent or a decomposing agent is replaced. This results in that its running cost becomes high. Although the combustion method is effective for the CVD waste gas treatment where a combustible gas is treated, it is not possible to treat the cleaning gas.

[0006]

This invention realizes a low running cost and a high removal rate of a toxic gas.

[0007]

[Means for Solving the Problems]

This invention provides a treatment method described below (1) and a treatment apparatus described below (2), and so the aforesaid problems can be solved.

[0008]

(1) An NF_3 waste gas treatment method characterized in that waste gas containing NF_3 is subjected to a thermal oxidative decomposition treatment and NF_3 remaining in the gas treated is detoxed.

(2) An NF_3 waste gas treatment system characterized by comprising an apparatus for subjecting a waste gas containing NF_3 to a thermal oxidative decomposition treatment and a detoxing apparatus for detoxing NF_3 remaining in the gas treated.

[0009]

A waste gas containing NF_3 i.e., an NF_3 waste gas (hereinafter referred to as a waste gas) in this invention may be any type of gas containing NF_3. For example, the NF_3 waste gas means a waste gas used in an apparatus using a cleaning gas containing at least NF_3 in a semiconductor manufacturing process. Further, the NF_3 waste gas means that it includes a reactive product composed of NF_3 generated as a result of cleaning treatment within the apparatus with cleaning gas and a substance to be cleaned present in the apparatus in addition to the waste gas of the process gas. Accordingly, detoxing of NF_3 in this invention involves a detoxing treatment for NF_3 derivatives.

[0010]

In this invention, the waste gas is directly subjected to the thermal oxidative decomposition treatment so that most of the substantial organic constituents are formed into CO_2 and water for the waste gas derived from the process gas, metal portions become metal oxide fine particles such as SiO_2, and F_2, NOx, etc. are generated for NF_3. Then, the treatment gas is washed with water, as desired, to remove fine particles, F_2, SiF_4, etc. through melting or winding. Next, the treatment gas is passed through an NF_3 detoxing apparatus filled with a detoxing agent to remove remained NF_3, NOx, etc. to provide a non-toxic treatment gas.

[0011]

This invention has an advantage in that an economic efficiency in treatment of NF_3 is improved because an amount of treating not-yet oxidized NF_3 at a later stage is substantially reduced by a method wherein waste gas is subjected to the thermal oxidative decomposition treatment, then the organic constituents contained in the waste gas are detoxed into water and CO_2, and most of NF_3, preferably more than 80% thereof, is oxidized.

[0012]

Detoxing agent used in this invention is not particularly limited but any type of known agent may be used, as long as it may have a function able to prevent NF_3 from being discharged into an environment as it is. Specific examples of detoxing agents include a chemical detoxing agent which chemically reacts with NF_3 to change a part or all of NF_3 into another compound to detox NF_3, a physical detoxing agent which physically adsorbs NF_3 therein and retains it, and their combined agents or the like.

[0013]

A chemical detoxing agent includes such a type that NF_3 is oxidized and decomposed to be changed into F_2 and NOx, and at the same time, chemically reacts with F_2. More preferably, a chemical detoxing agent includes metals such as Iron, manganese, copper, silicon, and titanium, or their oxides.

[0014]

A physical detoxing agent includes silica, activated carbon, alumina, and molecular sieve. A form of the detoxing agent is optional. Thread-like form, powder form and other materials, for example, complex material with cellulose or the like can be used. Normally, a container provided with a flow inlet for the gas subjected to the thermal oxidative decomposition treatment and a flow outlet for gas subjected NF_3 to detoxing treatment is filled or charged with a desired amount of the agent to form a detoxing apparatus.

[0015]

It is preferable that an operation be carried out under a condition where the detoxing apparatus is kept at a temperature of 300℃ or more when the chemical detoxing agent is used. Although it is preferable that this heating means be a heater and the like, the heating means may be implemented through heat exchanging with treated waste gas.

[0016]

Additionally, it is desirable that the treatment speed SV (a flow velocity), at the detoxing apparatus, of the gas subjected to the thermal oxidative decomposition treatment be 2000 1/h. The typical apparatus for discharging waste gas in this invention includes a CVD apparatus. The waste gas is constituted by a CVD waste gas derived from the process gas at the time of CVD processing and/or a cleaning waste gas at the time of cleaning operation.

[0017]

The process gases providing CVD waste gas are, for example, as an inorganic raw material, monosilane, disilane, dichlorosilane and etc., and as an organic raw material, TEOS (tetraethoxisilane), TMB (trimethoxybolan). These waste gases are used in one or more kinds in single or in combination. These waste gases include some thermal oxidative decomposable products such as their unreacted product or their derivatives, reacted decomposed product, for example, H_2, CO, alcohols such as C_2H_5OH, aldehyde such as CH_3CHO, and hydrocarbon such as C_2H_4. These waste gases are subjected to the thermal oxidative decomposition treatment to become mainly metal oxides such as SiO_2, and H_2O and CO_2. It is apparent that the thermal oxidative decomposition treatment defined herein includes a mere oxidization of substance that cannot be decomposed, that is, oxidization of unit such as hydrogen, metal or the like.

[0018]

The cleaning waste gas is composed of at least a reactive product between NF_2 and substance in CVD (such as not-yet discharged CVD processed substance and the like), SiF_4 and NF_3 derivative, for example, a cleaning gas and a substance in CVD physically cleaned with the cleaning gas and the like.

[0019]

The cleaning gas additionally includes CF_4, C_2F_6, SF_6 and ClF_3. A reaction condition for the thermal oxidative decomposition treatment and a waste gas feeding condition and the like in this invention are not restricted in particular. It is sufficiently applicable that the thermal oxidative decomposable products contained in the waste gas at least under co-existence of oxygen may be heated, oxidized and decomposed. Accordingly, when the waste gas is fed into the thermal oxidative decomposition apparatus, it is concurrently required that oxygen be present at the heating and oxidization reaction part. Although a status of oxygen in its presence is optional, it is preferable that this oxygen be fed as gas containing oxygen, for example, air or the like, together with waste gas. In addition, in order to adjust the conditions for the thermal oxidative decomposition, optional gas can be mixed with it. For example, it is assumed that inert gas such as nitrogen or the like is mixed. It is preferable that the oxygen be fed into a reaction part of the thermal oxidative decomposition apparatus under a three-ply structure such that the nitrogen gas encloses the waste gas and oxygen encloses these gases. Furthermore, it is also preferable that a concentric three ply structure of pipes be arranged at the thermal oxidative decomposition apparatus as a feeding part of these gases.

[0020]

In addition, although the heating means in the thermal oxidative decomposition apparatus is arbitrary, it is preferably desirable to employ a heating system with a heater in which temperature can be electrically controlled as described above and it is normally possible to arrange it within the wall of the reaction part. Additionally, a temperature at the reaction part is preferably in a range of 800 to 1000℃.

[0021]

In this invention, it is possible that the waste gas which is subjected to the thermal oxidative decomposition treatment is transferred as it is to a detoxing apparatus for detoxing NF_3 according to its composition or transferred to the detoxing apparatus after undergoing another optional treatment.

[0022]

In particular, it is preferable in this invention to contact the waste gas subjected to thermal oxidative decomposition treatment with water, that is, to apply the waste gas to the water washing process. With this arrangement, it is possible to remove metal oxide fine particles such as SiO_2 generated by the decomposition treatment through their enclosing operation, remove water soluble compound such as SiF_4 and F_3 through their solubility, cool the treated gas and the like. Although this method for water washing process is optional, it is preferable that it should be contacted with the process gas in its atomized state.

[0023]

The gas washed with water and then subjected to NF_3 detoxing treatment can be discharged into the environment or can be treated with another optional treatment as desired, for example, treated with a known adsorption process and the like. The optional gas discharging means, for example, the gas discharging pipe or the like can be arranged at the detoxing apparatus. In addition, discharging of washed water out of the system is performed by a water discharging means such as a water discharging pipe. The water washing means and the discharging pipe or the like may be arranged at the thermal oxidative decomposition apparatus or separately installed in its independent manner.

[0024]

This invention can be provided with a control apparatus operated in such a way that a series of the aforesaid treatment steps may be performed continuously and automatically and that a desired treatment condition can be properly selected. This control apparatus is usually communicated with various kinds of detector apparatuses, for example, a temperature sensor, pressure sensor, water-level sensor and the like and constructed such that a safe and optimum treatment is carried out.

[0025]

Since the thermal oxidative decomposition system in this invention oxidizes and decomposes waste gas under a high temperature and its treatment can be performed within a short period of time, even if a large amount of CVD waste gas is present, a more efficient treatment can be carried out. Furthermore, electricity, air, nitrogen and cooling water (also acting as cleaning water) for heating operation are present, the treatment can be performed with high efficiency. As a result, a less expensive running cost than that of applying only a dry adsorption method is attained. In addition, the thermal oxidative decomposition apparatus, a water washing part (gas cooling and solid material removing) as required and an NF_3 detoxing apparatus are connected in series, whereby acid gas is removed at the water washing part and thereafter NF_3 that could not be decomposed with the thermal decomposition apparatus can be removed completely by the NF_3 detoxing apparatus. In addition, about 80% of the fed NF_3 is removed by the thermal oxidative decomposition apparatus, so that a load on the NF_3 detoxing apparatus can be substantially reduced.

[0026]

[Operation]

This invention treats at first the waste gas including NF_3 cleaning gas discharged from the CVD process and the like with the thermal oxidative decomposition apparatus. The thermal oxidative decomposition apparatus oxidizes and decomposes at a temperature more than 800℃ and less than 1000℃ CVD waste gases such as silane and disilane, and NF_3.

[0027]

Then, an acid gas such as fluoric acid and SiO_2 are removed at the water washing part as desired. Lastly, NF_3 is made to react with metal oxides at the NF_3 detoxing apparatus under a condition of heated state of preferably 300℃ or more and removed, whereby the CVD waste gas and the NF_3 cleaning waste gas can be completely decomposed and removed.

[0028]

[Preferred Embodiment]

Referring to Fig. 1, a practical preferred embodiment of this invention will be described as follows. This invention is not limited to this preferred embodiment.

[0029]

Fig. 1 shows one example of the treatment system used in this invention, wherein an NF_3 waste gas treatment system 1 of this invention includes a thermal oxidative decomposition apparatus 2 and an NF_3 detoxing apparatus 3. The thermal oxidative decomposition apparatus 2 includes a gas feeding part 7 of a three-ply structure having concentrically arranged a waste gas inlet pipe 4 for feeding a CVD waste gas from a CVD apparatus, a nitrogen inlet pipe 5 for feeding nitrogen for adjusting oxidization of a waste gas and an air inlet pipe 6 for supplying oxygen to oxidize the thermal oxidative decomposable products in the waste gas. The thermal oxidative decomposition apparatus 2 includes a reaction part 11 having at its outer wall a ceramic heater 8 acting as a heat source for subjecting the waste gas in these mixed gases released from the gas feeding part to heating, oxidizing and decomposing treatment and having thermocouples 9, 10 to control its own temperature; a water washing part 13 for washing with water the gas to be treated including the thermal oxidative decomposable products generated at the reaction part 11 by cooling water 12; and a discharging pipe 14 for discharging water containing soluble substances such as F_2, and SiF_4, and SiO_2 outside the system.

[0030]

The NF_3 detoxing apparatus 3 is arranged at the rear stage of the thermal oxidative decomposition apparatus 2 and the treated gas washed with water is fed into the NF_3 detoxing apparatus 3 through a supply pipe 15. The NF_3 detoxing apparatus 3 is filled with metal oxide used for detoxing gas such as fed NF_3. The waste gas can be purified and detoxed by passing through the NF_3 detoxing apparatus 3, and then discharged through the arranged gas discharging pipe 16. Reference numerals 17 to 19 each denotes the sampling pipes A, B and C for sampling the waste gas, gas subjected to heating, oxidizing, decomposing and to water-washing, and gas treated with catalyst.

[0031]

[Experimental Example]

A treatment test was carried out with the apparatus shown in Fig. 1. An amount of waste gas including NF_3 and SiH_4 was 40L/min. The treatment condition for the thermal oxidative decomposition apparatus, was set such that a reaction temperature was 900℃, N_2 10 L/min., air for oxidation 20 L/min. and the cooling water 4L/min. A reaction temperature of the NF_3 detoxing apparatus was set to 300℃. The result will be indicated in Table 1. A, B and C in this table denote sampled pipes.

[0032]

Table-1 Unit: ppm

	NF_3			SiH_4		
	A	B	C	A	B	C
1 hour	5100	950	<10	3000	<5	<5
2 hours	5000	850	<10	2800	<5	<5
3 hours	5000	1000	<10	3100	<5	<5
4 hours	5000	850	<10	3000	<5	<5

[0033]

As indicated in Table-1, SiH_4 can be removed by the thermal oxidative decomposition apparatus, and NF_3 can also be removed by about 80 to 83%. The residual NF_3 is treated with the NF_3 detoxing apparatus at a rear stage, whereby the waste gas generated from CVD can be completely detoxed.

[0034]

[Effect of the Invention]

The waste gas treatment method of this invention reduces the running cost as compared with that of the adsorption process of the prior art and further attains a high efficient removal of a harmful gas. In addition, this invention is quite effective when the waste gas of the CVD apparatus operated in a sheet-like manner is treated, where a CVD waste gas and a cleaning waste gas are not separated completely and discharged.

[Brief Description of the Drawing]

[Fig. 1]

This is an explanatory figure of a NF_3 waste gas treatment system to which the method of the present invention is applied.

[Description of the Reference Numerals]

1 NF_3 waste gas treatment system
2 Thermal oxidative decomposition apparatus
3 NF_3 detoxing apparatus
4 Waste gas inlet pipe

5	Nitrogen inlet pipe
6	Air inlet pipe
7	Gas inlet part
8	Ceramic heater
9	Thermocouple
10	Thermocouple
12	Cooling water
13	Water washing part
14	Discharging pipe
15	Supply pipe
16	Discharging pipe
17	Sampling pipe A
18	Sampling pipe B
19	Sampling pipe C

DECLARATION

I, Kazuhiro ISHII , a national of Japan, c/o Asamura Patent Office of 331-340, New Ohtemachi Building, 2-1, Ohtemachi-2-chome, Chiyoda-ku, Tokyo, Japan do hereby solemnly and sincerely declare:-

1) THAT I am well acquainted with the Japanese language and English language, and
2) THAT the attached is a full, true, accurate and faithful translation into the English language made by me of Japanese Patent Application No. 9-4349.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 29th day of December , 2005 .

Kazuhiro ISHII

KANNO EXHIBIT 1001
Rossin v. Kanno
Contested Case 105,402

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[Date of Submission] January 14, 1997
[Addressee] Commissioner
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PROCESS FOR TREATING FLUORINE COMPOUND-CONTAINING GAS
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[Title of the Invention] PROCESS FOR TREATING FLUORINE COMPOUND-CONTAINING GAS

[Claims]

[Claim 1]

A process for treating a fluorine compound-containing gas, characterized by containing a step of contacting a gas stream containing at least one of a compound including two or more carbon atoms and fluorine atom(s), or a compound containing nitrogen atom(s) and fluorine atom(s) with a catalyst containing at least one of alumina, titania, silica and zirconia at a temperature of about 400 to 800°C in the presence of an effective amount of water vapor to convert the F in the gas stream to HF.

[Claim 2]

The process according to Claim 1, wherein the fluorine compound-containing gas includes a compound of C and F having two or more carbon atoms, or a compound of N and F.

[Claim 3]

The process according to Claim 1, wherein the catalyst further contains at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni.

[Claim 4]

A catalyst for decomposing fluorine compounds by treating a gas stream containing at least one of a compound of C and F having two or more carbon atoms, or a compound of N and F, said catalyst comprising alumina and titania, wherein the alumina is contained 75% by weight or more and 98% by weight or less, and the titania is contained 25% by weight or less and 2% by weight or more.

[Claim 5]

The catalyst according to Claim 4, wherein the catalyst further contains at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B.

[Claim 6]

The catalyst according to Claim 5, wherein the catalyst contains one or more oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in an amount of 0.1% by weight to 10% by weight based on the main weight of the aluminatitania catalyst.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a process for efficient decomposition treatment of a gas containing fluorine compounds such as C_2F_6, etc. at a low temperature and a catalyst material.

[0002]

[Prior Art]

Fluorine compound gases such as C_2F_6, etc. are used in a large amount as a semiconductor etchant, a semiconductor cleaner, etc. However, it was found that these compounds, once discharged into the atmosphere, turn into warming substances causing global warming. Post-treatment of these compounds after their use would be subject to a strict control in the future.

[0003]

By the way, gases such as C_2F_6, etc. have fluorine (F) in a large amount as a molecular constituting element. The fluorine is the highest in electronegativity among all the elements and forms chemically very stable substances. Particularly, C_2F_6 and the like are strong in intramolecular force and substances poor in reactivity. From these properties, a high temperature is necessary for decomposition and a large amount of energy is consumed therefor. Further, the decomposition reaction at the high temperature produces gases such as hydrogen fluoride, etc. which are large in corrosion rate of apparatus materials. It is thus in the current situations that no appropriate processes for such decomposition treatment are not available yet.

[0004]

As the decomposition treatment processes, there is proposing a combustion technology at a high temperature. But, according to this process, since a large amount of fuel is used, the energy efficiency is low. In addition, there is a problem of damage of furnace wall caused by halogen compounds produced by combustion at 1000°C or higher. Therefore, it is necessary a technology which can decompose at lower temperatures.

[0005]

As to the catalyst, JP-B-6-59388 discloses a TiO_2-WO_3 catalyst for decomposition of organic halogen compounds. The catalyst contains 0.1 to 20% by weight of W on the basis of TiO_2 (i.e. 92% to 99.96% of Ti by atom and 8 to 0.04% by atom of W) and had a decomposition rate of 99% at 375°C for a duration of 1,500 hours in treatment of CCl_4 in ppm order. Among organic halogen compounds, influences as catalyst poison are found not only in Cl but also in F, the latter is greater than the former. JP-B-6-59388 suggests that organic halogen compounds having a single carbon atom, such as CF_4, CCl_2F_2, etc. can be decomposed, but shows no examples of decomposition results of fluorine compounds. Further, generally speaking, organic halogen compounds having 2 carbon atoms are less decomposable than those having a single carbon atom.

JP-A-7-80303 discloses another Al_2O_3-ZrO_2-WO_3 catalyst for decomposition of fluorine compound gases. The catalyst is directed to combustion-decomposition of CFCs (chlorofluorocarbons) and has a decomposition rate of 98% for a duration of 10 hours in treatment of CFC-115 (C_2ClF_5) by combustion-decomposition reaction at

600°C. The disclosed process needs addition of hydrocarbons such as n-butane, etc. as a combustion aid, resulting in a higher treatment cost. Decomposition of compounds consisting only of carbon and fluorine such as C_2F_6, etc. are much less decomposable than CFC-115, but no examples of decomposition results of such compounds are shown therein.

[0006]

[Problem to be Solved by the Invention]

An object of the present invention is to provide a process for efficient decomposition treatment of a gas containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound having nitrogen atom(s) and fluorine atom(s) at a low temperature, and a catalyst therefore.

[0007]

[Means for Solving Problem]

The present inventors have studied decomposition treatment processes which are possible to decompose fluorine compound-containing gas at low temperatures with high efficiency and hardly provide corrosion of the apparatus by hydrogen fluoride freed as a decomposition product, and as a result, the present invention is attained.

[0008]

That is, it was found that by contacting a gas stream containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound having nitrogen atom(s) and fluorine atom(s) with a catalyst for decomposing specific fluorine compounds at about 400 to about 800°C in the presence of an efficient amount of water vapor, the fluorine in the gas stream can be converted to HF. As the decomposing catalyst, it is possible to use a catalyst which contains at least one kind selected from alumina, titania, silica and zirconia.

[0009]

As the fluorine compounds, there can be used those having C and F with two or more carbon atoms such as C_2F_6, etc., those having N and F such as NF_3, etc.

[0010]

Further, it was found that when at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni is added to the catalyst, it was possible to decompose the fluorine compound-containing gas with higher activity. These catalysts contains alumina, titania, silica, zirconia and oxide or oxides of at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in the form of a mixture or composite oxide. In the case of the catalyst containing alumina and titania, when alumina is 75% by weight or more and 98% by weight or less and titania is 25% by weight or less and 2% by weight or more, the effects are very great. Further, when the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P, and B is contained 0.1 to 10% by weight based on the main weight of the catalyst, the effects are great.

[0011]

As a result of various studies for developing decomposition catalysts for fluorine compound-containing gas, it was found that it is necessary to contain a metallic component for forming a bond to fluorine with a suitable strength. Particularly, in the case of a compound containing carbon and fluorine, since the molecule per se is stable, it was found that a catalyst containing a metallic component having a large fluoride forming enthalpy shows a high decomposition activity. When a too stable bond is formed, the activity lowers gradually because of non-release of the fluoride from the catalyst surface. On the other hand, when the bonding strength is too weak, a sufficient decomposition rate cannot be obtained. The gases used in the present invention such as C_2F_6 or the like are substances which have a strong intramolecular force and poor reactivity. In order to combust these gases, the temperature of 1500 to 2000°C is said to be necessary. We have found that the gases used in the present invention can be decomposed by even using alumina, titania, silica and zirconia singly as a catalyst, and in order to obtain higher decomposition rate, it is preferable to use a catalyst containing alumina and titania. The alumina seems to function for drawing the fluorine compound to the catalyst and the titania seems to function for separating the fluorine compound from the catalyst surface.

[0012]

The oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni seem to exhibit synergistic effects with alumina, titania, silica and zirconia. Further, the titania in the catalyst seems to contribute to the stabilitation.

[0013]

In the decomposition treatment process of the fluorine compound-containing gas of the present invention, it was found that the fluorine compound such as C_2F_6 or the like can be diluted with an inert gas. By diluting the concentration of the fluorine compound, the load for the catalyst is reduced, resulting in maintaining the decomposition activity for a long period of time. As the diluting gas, it is possible to use an inert gas such as Ar, N_2, He or the like.

[0014]

The fluorine-containing compounds used in the present invention are PFC (perfluorocompounds) such as C_2F_6, NF_3, etc. or FFC (fully fluorocompounds). Typical reactions can be shown below.

[0015]

$$C_2F_6 + 3H_2O \rightarrow CO + CO_2 + 6HF$$

$$C_2F_6 + 2H_2O + 1/2O_2 \rightarrow 2CO_2 + 6HF$$

$$NF_3 + 3H_2O \rightarrow NO_2 + 1/2\ O_2 + 6HF$$

It is desirable to add these fluorine compounds so as to make the amount of hydrogen atoms in the gas to be treated at least equal to the amount of fluorine atoms contained in the fluorine compound. By this, F in the compound becomes HF, and F in the decomposition products changes into hydrogen halide which is easy for after-treatment. As a hydrogen source, there can be used steam, hydrogen, a hydrocarbon, etc. In the case of using a hydrocarbon, the hydrocarbon can be combusted on the catalyst, thereby effectively reducing the heat energy to be supplied.

[0016]

By adding an oxidizing gas such as oxygen, etc. to the reaction gas, oxidation reaction of CO can be carried out at the same time. When the oxidation reaction of CO is incomplete, the decomposition product gas is brought into contact with the CO oxidizing catalyst, after removal of HF from the decomposition product gas, to convert CO to CO_2.

[0017]

By using the catalyst of the present invention, flons such as $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5, etc., substitute flons such as HFC 134a, etc. and compounds such as SF_6, etc. can be decomposed. Further, Cl in the compounds in the case of treating chlorine compounds is converted to HCl.

[0018]

The reaction temperature used in the present invention is preferably about 200° to about 800°C. Above the higher temperatures, a higher decomposition rate can be obtained, but the catalyst will be rapidly deteriorated, and also the corrosion rate of apparatus structural materials will be abruptly increased, whereas below the lower temperature, the decomposition rate will be lowered.

As the step of neutralizing and removing the formed HF, washing by spraying an alkaline solution is efficient and preferable because of less occurrence of clogging in pipes due to crystal deposition, etc. Bubbling of the decomposition product gas through the alkaline solution or washing with the alkaline solution through a packed column may be used.

[0019]

As the raw material for aluminum (Al) for preparing the catalyst of the present invention, γ-alumina and a mixture of γ-alumina and δ-alumina can be used. Particularly preferable method is to use boehmite, etc. as a raw material for Al to form an oxide through final firing.

[0020]

As the raw material for titanium (Ti) for preparing the catalyst of the present invention, there can be used titanium sulfate, titania sol, titanium slurry, etc.

[0021]

Further, as raw materials for the third metallic components such as silica (Si), magnesium (Mg), zirconium (Zr), etc., their various nitrates, ammonium salts, chlorides, etc. can be used.

[0022]

The catalyst of the present invention can be prepared by any of ordinary procedures for preparing catalysts, such as a precipitation method, an impregnation method, a kneading method, etc.

[0023]

The catalyst of the present invention can be used as such or upon molding into a granular form, a honeycomb form, etc. by a desired molding procedure such as extrusion molding, tabletting, tumbling granulation, etc., or as a coating on ceramic or metallic honeycombs or plates.

[0024]

The fluorine compound-containing gas treating process of the present invention can decompose the fluorine compounds in a lower temperature than other treating processes.

[0025]

In the case of treating fluorine compound-containing gas, there arises a problem of corrosion of apparatus materials caused by the acid component such as HF, etc. produced by decomposition. According to the present invention, since the temperature used is relatively low, the corrosion rate is slow, resulting in unnecessary for maintenance of the apparatus.

[0026]

The apparatus for practicing the fluorine compound-containing gas treating process of the present invention requires only a catalytic reactor for decomposing the fluorine compounds and an apparatus for neutralizing and removing acid components in the decomposition product gas, so that the apparatus can be minimized.

[0027]

[Mode for Carrying Out the Invention]

The present invention will be described in detail below, referring to Examples which are not limitative of the present invention.

[0028]

Fig. 1 shows an example of using the decomposition treatment process of the present invention fir a cleaning step in a plasma CVD apparatus in the semiconductor production process.

[0029]

The plasma CVD apparatus is an apparatus for vapor depositing a SiO_2 film on a semiconductor wafer surface. Since the SiO_2 film tends to deposit on the entire interior surfaces of the apparatus, and thus it is necessary to remove SiO_2 depositions from unwanted surfaces. To clean the SiO_2, C_2F_6 is used. Cleaning gas containing C_2F_6 is led to a CVD chamber to remove SiO_2 under plasma excitation. Then, the chamber is flushed with a N_2 gas, thereby diluting the concentration of C_2F_6 to about 3 to 5%, followed by discharge from the chamber at about 15 l./min.

[0030]

The discharged gas is admixed with air 3 to dilute C_2F_6. The diluted gas is further admixed with steam 4 to give a reaction gas 5, which is led to a decomposition step. The C2F6 concentration in the reaction gas is about 0.5%. In the decomposition step, the reaction gas 5 is contacted with a Al_2O_3 series catalyst at 700°C under the conditions of space velocity of 3000 per hour [space velocity (h^{-1}) = reaction gas flow rate (ml/h)/catalyst volume (ml)]. In that case, the reaction gas may be heated or the catalyst may be heated by an electric oven, etc. The resulting decomposition gas 6 is led to an exhaust gas washing step, where the decomposition gas 6 is sprayed with an aqueous alkaline solution to remove acid components from the decomposition gas 6 and the resulting exhaust gas 7 freed from the acid components is discharged to the system outside. The decomposition rate of C_2F_6 is obtained from the analysis data of the reaction gas 5 and the exhaust gas 7 using FID (flame ionization detector) gas chromatograph and TCD (thermal conductivity detector) gas chromatograph, and material balance at the inlet and the outlet.

[0031]

Hereinafter, the results obtained by examining activities of various fluorine compound decomposing catalysts are explained.

[0032]

[Example 1]

A C_2F_6 gas having a purity of 99% or more was diluted with air, and further admixed with steam to prepare a reaction gas. Steam for the admixture was prepared by feeding pure water into a reactor tube from the top at a flow rate of 0.11 ml/min. by a microtube pump and gasified. The reaction gas had a C_2F_6 concentration of about 0.5%. Then, the reaction gas was brought into contact with various catalysts heated to 700°C in the reactor tube at a space velocity of 3,000 h^{-1}.

[0033]

The reactor tube is a reactor tube manufactured by Inconel and having an inner diameter of 19 mm, where a catalyst bed is fixed at the center of the reactor tube and had an Inconel-made thermowell for a thermo couple, 3 mm in outer diameter, inside the catalyst bed. Decomposition product gas discharged from the catalyst bed was bubbled through an aqueous sodium chloride solution an then discharged as an exhaust gas. C_2F_6 decomposition rate was calculated by the following equation using FID gas chromatograph and TCD gas chromatograph:

[0034]

[Expression 1]

$$\text{Decomposition rate} = 1 - \frac{\text{Concentration of discharged fluorine compound}}{\text{Concentration of fed fluorine compound}} \times 100\ (\%)$$

[0035]

Hereinafter, preparation methods of various catalysts used for the tests under the above-mentioned conditions are shown.

[0036]

Catalyst 1 : Al_2O_3

Granular alumina (NKHD-24, trademark of a product commercially available from Sumitomo Chemical Co., Ltd., Japan) was pulverized, sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing (or calcining) at 700°C for 2 hours, and subjected to the tests.

[0037]

Catalyst 2 : TiO_2

Granular titania (CS-200-24, trademark of a product commercially available from Sakai Chemical Industry Co., Ltd., Japan) was pulverized, sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours, and subjected to the tests.

[0038]

Catalyst 3 : ZrO_2

200 g of zirconyl nitrate was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression

molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain zirconia grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0039]

Catalyst 4 : SiO_2

Granular silica (CARIACT-10, trademark of a product commercially available from Fuji Silysia Co., Ltd., Japan) was pulverized and sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours, and subjected to the tests.

[0040]

Catalyst 5 : TiO_2-ZrO_2

Granular titania (CS-200-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders was admixed with 78.3 g of zirconyl nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0041]

Catalyst 6 : Al_2O_3-MgO

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 56.4 g of magnesium nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0042]

Catalyst 7 : Al_2O_3-TiO_2

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 17.4 g of dried powders of a metatitanic acid slurry and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0043]

Catalyst 8 : Al_2O_3-SiO_2

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 13.2 g of dried powders of SiO_2 sol and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for

2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 mgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0044]

Test results of the above-mentioned catalysts 1 to 8 are shown in Fig. 2.

[0045]

[Example 2]

In this Example, effects of addition of the third elements were examined under the same conditions as in Example 1. Individual catalysts were prepared as follows.

[0046]

Catalyst 9 : Al_2O_3-TiO_2

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0047]

Catalyst 10 : Al_2O_3-TiO_2-ZrO_2

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours, to give Catalyst A. Then, 50 g of Catalyst A grains were impregnated with an aqueous solution of 6.7 g of zirconyl nitrate dihydrate in 90 g of H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0048]

Catalyst 11 : Al_2O_3-TiO_2-WO_3

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 6.5 g of ammonium paratungstate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0049]

Catalyst 12 : Al_2O_3-TiO_2-SiO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.5 g of 20 wt.% silica sol in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

Catalyst 13 : Al_2O_2-TiO_2-SnO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 5.6 g of tin chloride dihydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0050]

Catalyst 14 : Al_2O_3-TiO_2-CeO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 10.9 g of cerium nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

Catalyst 15 : Al_2O_3-TiO_2-MnO_2

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.2 g of manganese nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0051]

Catalyst 16 : Al_2O_3-TiO_2-Bi_2O_3

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.4 g of bithmus nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0052]

Catalyst 17 : Al_2O_3-TiO_2-NiO

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.3 g of nickel nitrate hexahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0053]

Catalyst 18 : Al_2O_3-TiO_2-BO_4

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 12.0 g of ammonium borate octahydrate in H_2O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0054]

Activities of the above-mentioned Catalysts 9-18 as well as that of Catalyst 1 in Example 1 are shown in Fig. 3.

[0055]

[Example 3]

In this Example, various catalysts are

prepared by changing the alumina raw material and the titania raw material, and activities are examined in the same manner as in Example 1.

[0056]

Catalyst 19 : Al_2O_3

Boehmite powders (PURAL SB, trademark of a product commercially available from Condea Co., Ltd.) were dried at 120°C for 2 hours. 200 g of the resulting dried powders were fired at 300°C for 0.5 hour and further fired at an elevated temperature of 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and tested.

[0057]

Catalyst 20 : $Al_2O_3-TiO_2$

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 200 g of the resulting dried powders were kneaded with 248.4 g of an aqueous 30% titanium sulfate solution, while adding about 200 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0058]

Catalyst 21 : AlO_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 200 g of the resulting dried powders were kneaded with about 100 g of an aqueous solution containing 78.6 g of 30% titania sol in pure water. After the kneading, the kneaded mixture was dried at 120°C for about 2 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0059]

[Example 4]

In this Example, catalysts are prepared by changing the composition of Al and Ti in Catalyst 20 in Example 3 and their activities are examined.

[0060]

Catalyst 22 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 48.8 g of an aqueous 30% titanium sulfate solution while adding about 150 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0061]

Catalyst 23 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 82.4 g of an aqueous 30% titanium sulfate solution while adding about 120 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0062]

Catalyst 24 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 174.4 g of an aqueous 30% titanium sulfate solution while adding about 70 g of pure water. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0063]

Catalyst 25 : Al_2O_3-TiO_2

Boehmite powders (PURAL SB) was dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 392g of 30% titania sol. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm^2. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0064]

Activities of the above-mentioned Catalysts 22-25 are examined in the same manner as in Example 1 and the results are shown in Fig. 5.

[0065]

[Example 5]

In this Example, sulfuric acid is added at the time of preparing a catalyst.

[0066]

Catalyst 26: Al_2O_3-TiO_2

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 150 g of the resulting dried powders, 58.8 g of 30% titania sol solution (CS-N, manufactured by Ishihara Sangyo Kaisha, Ltd.) and an aqueous solution of 44.8 g of 97% sulfuric acid solution diluted with 250 ml of pure water were added and kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The test conditions are the same as those of Example 1, except for changing the space velocity 1000 per hour. The test results were that the decomposition rate of C_2F_6 at the reaction temperature of 650°C was 80%.

[0067]

[Effects of the Invention]

According to the present invention, fluorine-containing gases such as C_2F_6, NF_3, etc. can be subjected to decomposition treatment efficiently.

[Brief Description of the Drawings]

[Fig. 1]

A block diagram showing a treatment process according to one embodiment of the present invention.

[Fig. 2]

A graph showing performances of various catalysts for decomposing fluorine compounds.

[Fig. 3]

A graph showing performances of various catalysts for decomposing fluorine compounds.

[Fig. 4]

A graph showing performances of various catalysts for decomposing fluorine compounds.

[Fig. 5]

A graph showing performances of various catalysts for decomposing fluorine compounds.

[Description of Reference Numerals]

1 ... C_2F_6, 2 ... N_2, 3 ... air, 4 ... steam,

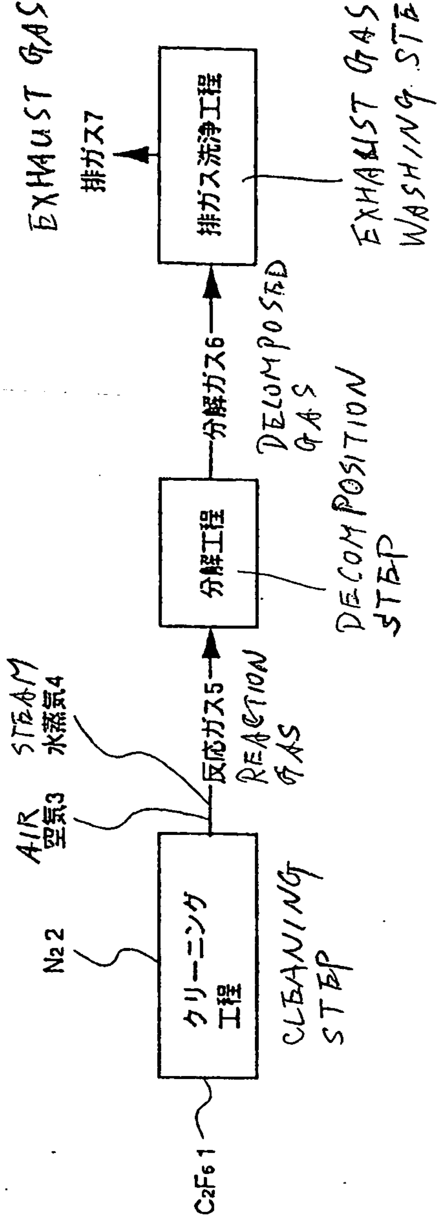
5 ... reaction gas, 6 ... decomposed gas, 7 ... exhaust gas

【書類名】　図面　[Kind of Document] Drawings

【図１】

[FIG. 1]

図 1



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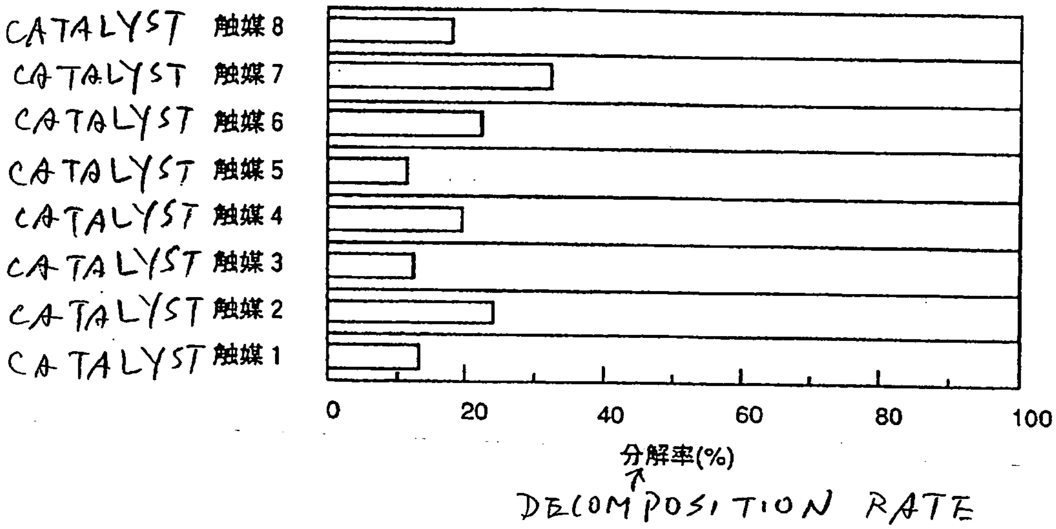
【図２】

[FIG. 2]

図　２



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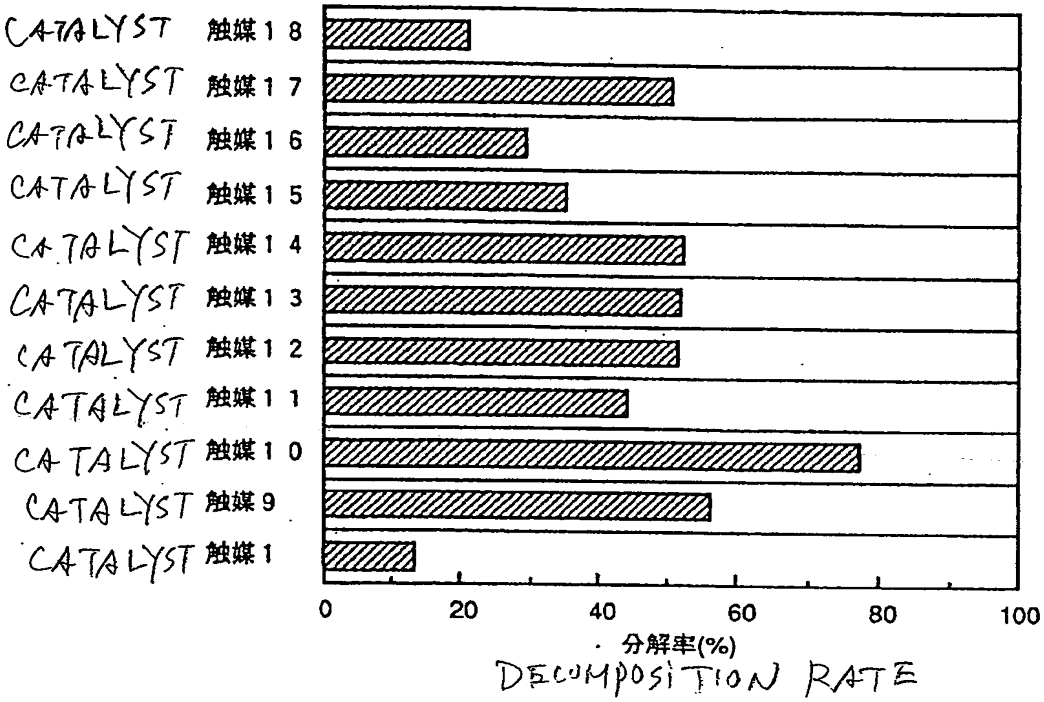
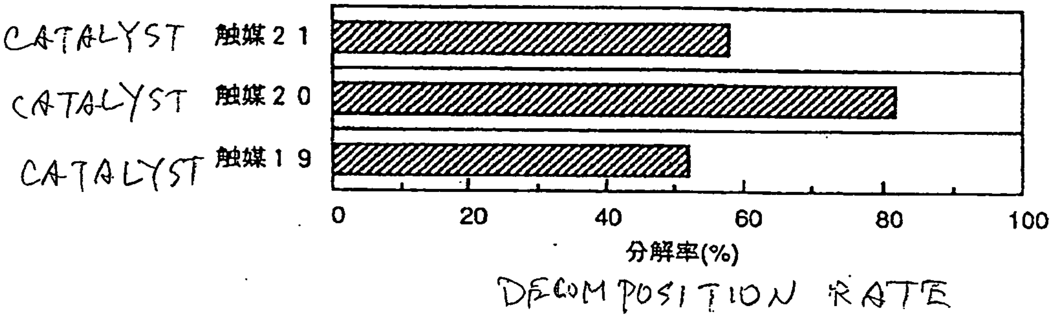
【図３】

[FIG. 3]
図 3



【図４】

[FIG. 4]
図 4



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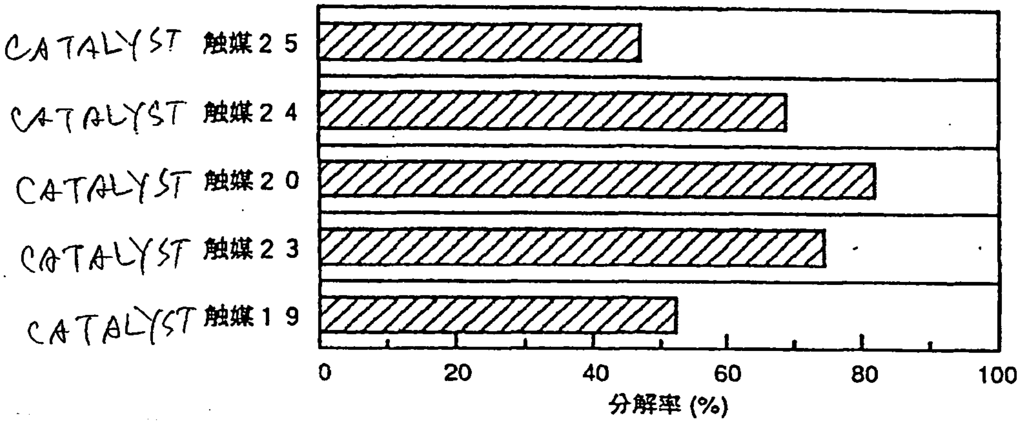
【図５】

[Fig. 5]

図　5



DECOMPOSITON RATE

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[Title of Document] Abstract

[Abstract]

[Problem] To provide a decomposition treatment process for decomposing fluorine compound-containing gas such as C_2F_6 and the like efficiently and catalyst therefore.

[Solution]

A gas stream containing at least one of compounds having two or more carbon atoms and fluorine atom(s) such as C_2F_6 and the like, or compounds of nitrogen atom(s) and fluorine atom(s) is contacted with a catalyst comprising at least one of alumina, titania, silica and zirconia at a temperature of about 400° to about 800°C in the presence of an effective amount of water vapor to convert F in the gas stream to HF.

[Advantages]

Fluorine compound-containing gas can be subjected to decomposition treatment with good efficiency.

[Selected Drawing] Fig. 2